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(54) **Method of preparing a superconductive material.**

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Description

This invention relates to a method of preparing a superconductive material.

There are now increasing reports concerning metal oxides exhibiting superconductivity. Examples of such oxides include $(\text{La}_{0.9}\text{Sr}_{0.1})_2\text{CuO}_4$, $(\text{La}_{0.9}\text{Ba}_{0.1})_2\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$. These superconductive metal oxides of a ceramic type have thus far been prepared by a vapor phase method or a tape cast method. The former method requires the use of a large, elaborate apparatus. Further, the vapor phase method cannot prepare a superconductive material having a large surface area. The latter method fails to give films with a thin, uniform thickness of less than 20 μm (micrometer). Additionally, the tape cast method requires a high sintering temperature. From the stand point of actual industrial applications, it is highly desirable to provide superconductive materials having various shapes such as thin films, thin wires, tubes and rods. With the known methods, however, it is impossible or extremely difficult to produce ceramic type superconductive materials with such shapes.

With the foregoing problems in view the present invention provides a method of preparing a superconductive material having a superconductive metal oxide layer provided on a substrate, said method comprising the steps of:

- (a) providing a non-aqueous solution containing a blend of metal compounds having a composition corresponding to that of the metals in the superconductive metal oxide, said metal compounds being selected from salts, chelates, halides, hydroxides, peroxides and oxides of said metals;
- (b) applying said solution on the substrate to form a liquid film;
- (c) drying said liquid film; and
- (d) calcining said dried film to convert said metal compounds into a superconductive metal oxide layer.

The present invention provides a superconductive material including a substrate and a superconductive metal oxide layer provided over at least a portion of the surface of the substrate. The superconductive material is produced by a method including the following steps.

- (a) Preparation of Coating Solution:

In this step a coating solution containing a blend of metal compounds is prepared. The metal compounds are salts, chelates, halides, hydroxides, peroxides and oxides of the selected metals. The contents of the metal compounds in the blend are so determined as to provide the desired superconductive oxide of the metals. That is, the molar ratios of the metal compounds in the blend are equivalent to those of the metals in the superconductive oxide. For example, if a superconductive metal oxide having a formula $(\text{La}_{0.9}\text{Sr}_{0.1})_2\text{CuO}_4$ is intended, a coating solution containing La, Sr and Cu compounds and having contents of the La and Sr compounds of 1.8 and 0.2 moles, respectively, per mole of the Cu compound is used.

Any metal compound of the above-defined kind may be used as long as it gives an oxide upon calcination. A metal compound which is decomposed at a temperature of preferably 1000°C or below, more preferably 200-900°C is suitably used. Examples of suitable metal compounds include metal salts of organic or inorganic acids such as naphthenic acid, 2-ethyl hexanoic acid, caprylic acid, stearic acid, lauric acid, butyric acid, propionic acid, oxalic acid, citric acid, lactic acid, phenol, catechol, benzoic acid, salicylic acid, ethylenediaminetetracetic acid, nitric acid, carbonic acid, and hydrochloric acid; and chelate compounds such as metal acetylacetonates.

Above all, metal compounds having an oxygen atom directly bonded to the metal, such as organic acid salts, acetylacetonates and nitrates, are preferably used because of the ease in which they may be converted into metal oxides upon calcination. Organic or inorganic metal compounds used as starting metal compounds and containing no oxygen directly bonded to the metals may be converted into such preferred metal compounds when used in conjunction with a suitable solvent such as an organic acid, an alcohol, acetylacetone or nitric acid.

Any non-aqueous solvent may be used as long as it can dissolve the metal compounds. Examples of suitable solvents include hydrocarbons such as hexane, octane, benzene, toluene and tetralin; alcohols such as methanol, ethanol, propanol, butanol and amyl alcohol; ketones such as acetone, methyl ethyl ketone and acetylacetone; ethers such as dibutyl ether; aldehydes such as acetaldehyde and benzaldehyde; organic acids such as formic acid, acetic acid, propionic acid, butyric acid, caprylic acid, lauric acid, stearic acid, naphthenic acid, linoleic acid, oleic acid, oxalic acid, citric acid, lactic acid, phenol and p-toluic acid; esters such as butylbutylate; amines such as dimethylamine and aniline; amides such as N-methylacetamide and formamide; sulfur compounds such as dimethylsulfoxide; and heterocyclic compounds such as pyridine and furfural. These solvents may be used singly or in combination of two or more and suitably selected according to the metal compounds to be dissolved.

The coating solution may be prepared by, for example, dissolving a blend of metal compounds in a non-aqueous solvent.

Alternatively, each metal compound is first dissolved in a suitable solvent and, then, the resultant solutions

are mixed in suitable proportions. The concentration of the coating solution is not specifically limited but is, generally, 3-40 % by weight. The coating solution may further contain suitable additives such as a viscosity controlling agent, e.g. polyvinyl alcohol.

(b) Liquid Film Forming Step:

The coating solution obtained in the above step (a) is applied on at least a portion of the surface of a substrate to form a liquid film over that surface. The substrate may be formed of a metal or a metal alloy such as copper, titanium, lead or a stainless steel, a metal oxide such as alumina, zirconia or titania, or a ceramic material such as silicon carbide or graphite. The shape of the substrate is not specifically limited. Substrates having curved or flat surfaces, such as plates, wires, coils, fibers, fabrics, tubes, blocks and rods may be used. Porous substrate may also be used.

Coating of the coating solution may be performed by any suitably way such as by a dip coating, spray coating or brush coating method.

(c) Drying of Liquid Film:

The substrate having a coated liquid film is then dried at room or an elevated temperature under ambient or a reduced pressure. It is not necessary to completely dry the film since the drying step is followed by a calcination step at an early stage of which drying may be completed.

(d) Calcination Step:

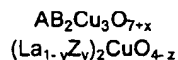
The dried (or semidried) film containing the metal compounds and formed on the substrate is subjected to calcination to convert the metal compounds into the desired superconductive oxide of the metals.

The calcination temperature varies with the kind of the superconductive oxide, but generally in the range of 500-1000 °C. When the metal compounds are organic compounds, they are decomposed or oxidized at temperatures of 200-500 °C and crystallization or superconductive metal oxide forming reaction takes place at temperatures of 500-1000 °C. Inorganic metal compounds such as metal nitrates, hydroxides, carbonates or halides are decomposed and oxidized to form superconductive metal oxides at temperatures of 1000 °C or below.

The calcination is preferably performed for 0.5 hour or more, more preferably 1-72 hours. The calcination step and the above-described drying step may be conducted separately or continuously. The atmosphere in which the calcination is performed may be, for example, air, oxygen, nitrogen or argon. Calcination in an oxygen-free atmosphere should be followed by calcination in oxygen-containing atmosphere at 500-1000 °C. In the calcination step, pressurized condition, ambient pressure or reduced pressure may be used.

The calcination product is then allowed to be cooled to room temperature to obtain a superconductive composite material having a superconductive metal oxide layer provided over the surface of the substrate. The method of the present invention can form superconductive composite materials having a superconductive layer with a thickness of 0.01-20 μm, especially 0.1-10 μm. The thickness of the superconductive layer may be controlled by adjusting the concentration of the metal compounds in the coating solution or by repeating the coating and calcination steps suitable times.

The method of the present invention is particularly suited for the production of superconductive materials having a superconductive layer of the following oxides. However, the present invention is applicable to any other superconductive metal oxides.



In the above formulae:

A : Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb, Lu, or a mixture of two or more thereof;

B : Ba, Sr, Ca or a mixture of two or more thereof;

x : a number greater than -1 but less than +1;

Z : Ba, Sr, Ca or a mixture of two or more thereof,

y : a number greater than 0 but not greater than 0.2; and

z : a number less than 1 but not less than 0.

The following examples will further illustrate the present invention.

Example 1

5 Metal compounds: lanthanum naphthenate (La 1.85)
 (Molar ratio strontium naphthenate (Sr 0.15)
 of metal) copper naphthenate (Cu 1.00)

10 Solvent: butanol

 Concentration
 of metal compounds: 10 % by weight

15 Substrate: alumina thin plate

20 Calcination:
 Atmosphere: air
 Temperature: 900 °C
 Time: 0.5 hour

25 Number of repetition: 10 times

30 Critical temperature:
 On set: 30 K
 Perfect superconductive: 10 K

35 The metal compounds shown above were mixed with each other and the mixture dissolved in the above
 solvent to give a coating solution having the total metal compounds concentration shown above and having
 the molar ratio of the metals as shown above. The coating solution was applied on the substrate shown above
 by immersing the substrate in the coating solution and the coat was dried in the air. Then the substrate having
 the dried coat was calcined under the conditions shown above. The immersing, drying and calcining steps were
 repeated 10 times to give a superconductive material whose electrical resistivity was abruptly decreased at
 the temperature (on set) shown above and which exhibited perfect superconductivity at the temperature shown
 above.

40 The above procedure was repeated in the same manner as described using an alumina bar (diameter 1
 mm) in place of the alumina plate as a substrate. The resultant superconductive composite materials showed
 similar critical temperature.

45 The electrical conductivity was measured by the four termini method in which four spaced apart electrodes
 with about 2 mm distance were provided on the superconductive layer by coating a silver paste thereon.

50 Examples 2-17 were conducted to prepare various superconductive materials under conditions as sum-
 marized below. In each of Examples 2-17, the procedure including coating, drying and 1st stage calcination
 steps was repeated in the number indicated below. Thereafter, the 2nd stage calcination was performed in an
 oxygen-containing atmosphere. The calcined product was then gradually cooled to room temperature.

55

Example 2

Metal compounds: lanthanum caprylate (La 1.90)
 (Molar ratio of metal) barium butyrate (Ba 0.05)
 strontium naphthenate (Sr 0.05)
 copper propionate (Cu 1.00)

10

Solvent: benzene/acetone/propionic acid
 (1:1:1)

15

Concentration
 of metal compounds: 15 % by weight

20

Substrate: zirconia thin plate stabilized
 with yttrium

25

Calcination:

	1st Stage	2nd Stage
Atmosphere:	air	oxygen
Temperature:	800 °C	800 °C
Time:	2 hours	5 hours

30

Number of repetition: 10 times

35

Critical temperature:

On set: 27 K
 Perfect superconductive: 10 K

40

45

50

55

Example 3

5 Metal compounds: yttrium butyrate (Y 1.00)
 (Molar ratio barium butyrate (Ba 2.00)
 of metal) copper butyrate (Cu 3.00)

10 Solvent: propionic acid/ethanol/acetone
 (1:1:1)

15 Concentration
 of metal compounds: 10 % by weight

20 Substrate: alumina tube

 Calcination:

	1st Stage	2nd Stage
25 Atmosphere:	air	oxygen
Temperature:	500 °C	800 °C
Time:	1 hour	2 hours

30 Number of repetition: 15 times

 Critical temperature:

35 On set:	95 K
Perfect superconductive:	18 K

Example 4

40 Metal compounds: lanthanum nitrate (La 1.90)
 (Molar ratio calcium nitrate (Ca 0.10)
 of metal) copper nitrate (Cu 1.00)

45 Solvent: acetylacetone/methanol (1:9)

50

55

Concentration

of metal compounds: 20 % by weight

5

Substrate: SiC fiber

Calcination:

10

	1st Stage	2nd Stage
Atmosphere:	reduced pressure	oxygen
Temperature:	900 °C	570 °C
Time:	5 min.	2 hours

15

Number of repetition: 8 times

20

Critical temperature:

On set: 32 K

Perfect superconductive: 15 K

25

Example 5

30

Metal compounds: yttrium acetylacetonate (Y 1.00)
 (Molar ratio of metal) barium acetylacetonate (Ba 2.00)
 copper acetylacetonate (Cu 3.00)
 Solvent: pyridine/propionic acid (2:1)

35

Concentration

of metal compounds: 10 % by weight

40

Substrate: zirconia thin plate stabilized
 with yttrium

Calcination:

45

	1st Stage	2nd Stage
Atmosphere:	argon	oxygen
Temperature:	800 °C	800 °C
Time:	1 hour	2 hours

50

Number of repetition: 10 times

55

Critical temperature:

On set: 90 K

Perfect superconductive: 20 K

Example 6

Metal compounds: yttrium stearate (Y 1.00)
(Molar ratio of metal) barium naphthenate (Ba 2.00)
copper naphthenate (Cu 3.00)
Solvent: propionic acid/butanol (1:1)

Concentration of metal compounds: 20 % by weight

Substrate: zirconia thin plate stabilized
with yttrium

Calcination:

	1st Stage	2nd Stage
Atmosphere:	argon	oxygen
Temperature:	500 °C	800 °C
Time:	0.5 hour	2 hours

Number of repetition: 10 times

Critical temperature:

On set: 90 K

Perfect superconductive: 23 K

Example 7

5 Metal compounds: yttrium naphthenate (Y 1.00)
 (Molar ratio barium naphthenate (Ba 2.00)
 of metal) copper naphthenate (Cu 3.00)

10 Solvent: toluene or butanol

15 Concentration
 of metal compounds: 20 % by weight

20 Substrate: silver thin plate

25 Calcination:

	1st Stage	2nd Stage
Atmosphere:	air	oxygen
Temperature:	500 °C	800 °C
Time:	0.5 hour	24 hours

30 Number of repetition: 10 times

35 Critical temperature:

On set:	80 K
Perfect superconductive:	20-45 K

Example 8

40 Metal compounds: yttrium caprylate (Y 1.00)
 (Molar ratio barium caprylate (Ba 2.00)
 of metal) copper caprylate (Cu 3.00)

45 Solvent: propionic acid/butanol (1:1)

Concentration
of metal compounds: 20 % by weight

5

Substrate: silver wire

Calcination:

10

	1st Stage	2nd Stage
Atmosphere:	argon	oxygen
Temperature:	500 °C	800 °C
Time:	0.5 hour	24 hours

15

Number of repetition: 10 times

20

Critical temperature:

On set: 80 K
Perfect superconductive: 25 K

25

Example 9

Metal compounds:	yttrium laurate	(Y 1.00)
(Molar ratio	barium laurate	(Ba 2.00)
of metal)	copper laurate	(Cu 3.00)

30

Solvent: propionic acid/toluene (1:1)

35

Concentration
of metal compounds: 20 % by weight

40

Substrate: silver-coated copper wire

Calcination:

45

	1st Stage	2nd Stage
Atmosphere:	air	oxygen
Temperature:	700 °C	800 °C
Time:	0.5 hour	24 hours

50

Number of repetition: 10 times

55

Critical temperature:

On set: 85 K

5 Perfect superconductive: 20 K

Example 10

10 Metal compounds: yttrium stearate (Y 1.00)
 (Molar ratio barium stearate (Ba 2.00)
 of metal) copper stearate (Cu 3.00)

15 Solvent: propionic acid/toluene (1:1)

Concentration
 20 of metal compounds: 20 % by weight

Substrate: platinum thin plate

25 Calcination:

	1st Stage	2nd Stage
Atmosphere:	air	oxygen
30 Temperature:	700 °C	800 °C
Time:	0.5 hour	24 hours

35 Number of repetition: 10 times

Critical temperature:

40 On set: 80 K

Perfect superconductive: 20 K

Example 11

45 Metal compounds: holmium naphthenate (Ho 1.00)
 (Molar ratio barium naphthenate (Ba 2.00)
 of metal) copper naphthenate (Cu 3.00)

50 Solvent: butanol or toluene

55

Concentration

of metal compounds: 20 % by weight

5 Substrate: zirconia thin plate stabilized
with yttrium

Calcination:

10		1st Stage	2nd Stage
	Atmosphere:	air	oxygen
	Temperature:	700 °C	800 °C
15	Time:	0.5 hour	24 hours

Number of repetition: 10 times

20 Critical temperature:

On set: 75 K

Perfect superconductive: 30 K

25 Example 12

30	Metal compounds:	heavy rare earth naphthenates
	(molar ratio	(heavy rare earth* 1.00)
	of metal)	barium naphthenate (Ba 2.00)
		copper naphthenate (Cu 3.00)

35 (Heavy rare earth : 44 % Er, 40 % Yb,
balance Lu and Ho)

40 Solvent: butanol or toluene

Concentration

45 of metal compounds: 20 % by weight

Substrate: zirconia thin plate stabilized
50 with yttrium

55

Calcination:

		1st Stage	2nd Stage
5	Atmosphere:	air	oxygen
	Temperature:	700 °C	800 °C
	Time:	0.5 hour	24 hours

10 Number of repetition: 10 times

Critical temperature:

15 On set: 80 K
Perfect superconductive: 30 K

Example 13

20

	Metal compounds:	yttrium nitrate	(Y 1.00)
	(Molar ratio	barium nitrate	(Ba 2.00)
25	of metal)	copper nitrate	(Cu 3.00)

Solvent: dimethylsulfoxide

30

Concentration
of metal compounds: 20 % by weight

35 Substrate: zirconia thin plate stabilized
with yttrium

40 Calcination:

		1st Stage	2nd Stage
	Atmosphere:	air	oxygen
	Temperature:	900 °C	800 °C
45	Time:	5 min.	24 hours

Number of repetition: 10 times

50

Critical temperature:

55 On set: 80 K
Perfect superconductive: 30 K

Example 14

Metal compounds: yttrium nitrate (Y 1.00)
 5 (Molar ratio barium nitrate (Ba 2.00)
 of metal) copper nitrate (Cu 3.00)

10 Solvent: formamide

Concentration
 of metal compounds: 20 % by weight
 15

Substrate: strontium titante thin plate

20 Calcination:

	1st Stage	2nd Stage
Atmosphere:	air	oxygen
25 Temperature:	900 °C	800 °C
Time:	5 min.	24 hours

Number of repetition: 10 times
 30

Critical temperature:

On set: 70 K

35 Perfect superconductive: 30 K

Example 15

Metal compounds: yttrium nitrate (Y 1.00)
 40 (Molar ratio barium nitrate (Ba 2.00)
 of metal) copper nitrate (Cu 3.00)

45 Solvent: N-methylacetamide

Concentration
 of metal compounds: 10 % by weight
 50

Substrate: barium titante thin plate

55

Calcination:

		1st Stage	2nd Stage
5	Atmosphere:	air	oxygen
	Temperature:	900 °C	800 °C
	Time:	5 min.	24 hours

10 Number of repetition: 20 times

Critical temperature:

15 On set: 80 K
 Perfect superconductive: 35 K

Example 16

20 Metal compounds: yttrium nitrate (Y 1.00)
 (Molar ratio barium nitrate (Ba 2.00)
 of metal) copper nitrate (Cu 3.00)

 Solvent: pyridine/propionic acid (2:1)

30 Concentration
 of metal compounds: 10 % by weight

35 Substrate: strontium titante thin plate

Calcination:

		1st Stage	2nd Stage
40	Atmosphere:	air	oxygen
	Temperature:	900 °C	800 °C
	Time:	5 min.	24 hours

45 Number of repetition: 20 times

Critical temperature:

50 On set: 80 K
 Perfect superconductive: 30 K

55

Example 17

5 Metal compounds: yttrium acetylacetonate (Y 1.00)
 (Molar ratio barium acetylacetonate (Ba 3.00*)
 of metal) copper acetylacetonate (Cu 4.30*)

10 Solvent: pyridine/propionic acid (5:3)

Concentration
 of metal compounds: 9 % by weight

15 Substrate: zirconia thin plate stabilized
 with yttrium

20 (*: Since barium and copper are also reacted with the
 yttrium contained in the substrate, the amount of
 the barium acetylacetonate and copper acetyl-
 25 acetate are increased. The final superconduc-
 tive layer has a composition $\text{YBa}_2\text{Cu}_3\text{O}_7$.)

30 Calcination:

	1st Stage	2nd Stage
Atmosphere:	air	oxygen
Temperature:	500 °C	950 °C
35 Time:	10 min.	20 min.

40 Number of repetition: 20 times

Critical temperature:

On set: 97 K
 45 Perfect superconductive: 89 K

50 Claims

1. A method of preparing a superconductive material having a superconductive metal oxide layer provided on a substrate, said method comprising the steps of:
- (a) providing a non-aqueous solution containing a blend of metal compounds having a composition corresponding to that of the metals in the superconductive metal oxide, said metal compounds being selected from salts, chelates, halides, hydroxides, peroxides and oxides of said metals;
 - 55 (b) applying said solution on the substrate to form a liquid film;
 - (c) drying said liquid film; and
 - (d) calcining said dried film to convert said metal compounds into a superconductive metal oxide layer.

2. A method as claimed in Claim 1, wherein said substrate is in the form of a wire or a plate.
3. A method as claimed in Claim 1 or Claim 2, wherein said metal compounds are compounds capable of forming oxides upon calcination at 1000°C or less.
- 5 4. A method as claimed in Claim 3, wherein said metal compounds are naphthenates, octylates, caprylates, stearates, laurates, butyrates, propionates, oxalates, citrates, lactates, benzoates, salcicates, ethylene-diaminetetracetates, nitrates, carbonates, hydrochlorides or acetylacetonates of said metals.
- 10 5. A method as claimed in Claim 3 or Claim 4, wherein step (d) is performed at a temperature of 500-1000°C.
6. A method as claimed in Claim 5, wherein step (d) is performed in an oxygen-containing atmosphere for from 0.5 hour or more.
- 15 7. A method as claimed in Claim 6, wherein the calcination in the oxygen-containing atmosphere is preceded by calcination in an oxygen-free atmosphere.
8. A method as claimed in any preceding claim, wherein steps (a) to (d) are repeated until said superconductive layer has a thickness of 0.01-20 µm.
- 20 9. A method as claimed in any preceding claim, wherein said solution contains a first compound selected from Y compounds, La compounds, Nd compounds, Sm compounds, Eu compounds, Gd compounds, Dy compounds, Ho compounds, Er compounds, Yb compounds, Lu compounds and mixtures thereof, a second compound selected from Ba compounds, Sr compounds, Ca compounds and mixtures thereof and a Cu compound so that said superconductive metal oxide has the formula:
$$AB_2Cu_3O_{7+x}$$
wherein A stands for Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb, Lu, or a mixture of two or more thereof, B stands for Ba, Sr, Ca or a mixture of two or more thereof, and x stands for a number greater than -1 but less than +1.
- 25 10. A method as claimed in any one of Claims 1-8, wherein said solution contains a La compound, a compound selected from Ba compounds, Sr compounds, Ca compounds and mixtures thereof and a Cu compound, so that said superconductive metal oxide has the formula:
$$(La_{1-y}Z_y)_2CuO_{4-z}$$
wherein Z stands for Ba, Sr, Ca or a mixture of two or more thereof, y is greater than 0 but not greater than 0.2 and z is a number less than 1 but not less than 0.
- 30 11. A method as claimed in any preceding claim, wherein said substrate is formed of a metal, metal oxide or a ceramic.

40 Patentansprüche

1. Verfahren zur Herstellung eines supraleitenden Materials, bei dem eine supraleitende Metalloxidschicht auf ein Substrat aufgebracht worden ist, wobei das Verfahren die folgenden Schritte umfaßt:
 - 45 (a) Zubereitung einer nichtwäßrigen Lösung, die bei einer Zusammensetzung, die der der Metalle im supraleitenden Metalloxid entspricht, eine Mischung von Metallverbindungen enthält, wobei die Metallverbindungen unter Salzen, Chelaten, Halogeniden, Hydroxiden, Peroxiden und Oxiden der Metalle auszuwählen sind;
 - (b) Aufbringen der Lösung auf das Substrat zur Bildung eines Flüssigkeitsfilms;
 - 50 (c) Trocknen des Flüssigkeitsfilms und
 - (d) Kalzinieren des getrockneten Films zur Umwandlung der Metallverbindungen in eine supraleitende Metalloxidschicht.
2. Verfahren nach Anspruch 1, bei dem das Substrat die Form eines Drahts oder einer Platte aufweist.
- 55 3. Verfahren nach Anspruch 1 oder 2, bei dem es sich bei den Metallverbindungen um Verbindungen handelt, die durch Kalzinierung bei 1 000 °C oder darunter Oxide bilden können.
4. Verfahren nach Anspruch 3, bei dem es sich bei den Metallverbindungen um Naphthenate, Octylate,

Caprylate, Stearate, Laureate, Butyrate, Propionate, Oxalate, Citrate, Lactate, Benzoate, Salicylate, Ethylendiamintetraacetate, Nitrate, Carbonate, Hydrochloride oder Acetylacetonate der Metalle handelt.

5. Verfahren nach Anspruch 3 oder 4, bei dem der Schritt (d) bei einer Temperatur zwischen 500 und 1 000 °C durchgeführt wird.
6. Verfahren nach Anspruch 5, bei dem der Schritt (d) in einer sauerstoffhaltigen Atmosphäre über einen Zeitraum von 0,5 Stunden oder mehr ausgeführt wird.
7. Verfahren nach Anspruch 6, bei dem vor der Kalzinierung in der sauerstoffhaltigen Atmosphäre die Kalzinierung in einer sauerstofffreien Atmosphäre erfolgt.
8. Verfahren nach einem der vorstehenden Ansprüche, bei dem die Schritte (a) bis (d) so lange wiederholt werden, bis die supraleitende Schicht eine Dicke von 0,01-20 µm aufweist.
9. Verfahren nach einem der vorstehenden Ansprüche, bei dem die Lösung eine erste Verbindung, die unter Y-Verbindungen, La-Verbindungen, Nd-Verbindungen, Sm-Verbindungen, Eu-Verbindungen, Gd-Verbindungen, Dy-Verbindungen, Ho-Verbindungen, Er-Verbindungen, Yb-Verbindungen und Lu-Verbindungen und Gemischen davon ausgewählt wurde, sowie eine zweite Verbindung, die unter Ba-Verbindungen, Sr-Verbindungen und Ca-Verbindungen sowie Gemischen davon ausgewählt wurde, und eine Cu-Verbindung enthält, so daß das supraleitende Metalloxid die folgende Formel aufweist:

$$AB_2Cu_3O_{7+x}$$
in der A für Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb, Lu oder ein Gemisch von zwei oder mehr dieser Komponenten, B für Ba, Sr, Ca oder ein Gemisch aus zwei oder mehr dieser Komponenten und x für eine Zahl steht, die größer als -1, jedoch kleiner als +1 ist.
10. Verfahren nach einem der vorstehenden Ansprüche 1 bis 8, bei dem die Lösung eine La-Verbindung, eine unter Ba-Verbindungen, Sr-Verbindungen, Ca-Verbindungen und Gemischen davon ausgewählte Verbindung sowie eine Cu-Verbindung enthält, so daß das supraleitende Metalloxid die folgende Formel aufweist:

$$(La_{1-y}Z_y)_2CuO_{4-z}$$
in der Z für Ba, Sr, Ca oder ein Gemisch von zwei oder mehr dieser Komponenten steht und y größer als 0, jedoch nicht größer als 0,2 und z eine Zahl ist, die kleiner als 1, jedoch nicht kleiner als 0 ist.
11. Verfahren nach einem der vorstehenden Ansprüche, bei dem das Substrat aus einem Metall, Metalloxid oder aus Keramik geformt wird.

Revendications

1. Procédé pour préparer un matériau supraconducteur ayant une couche d'oxyde métallique supraconducteur déposée sur un substrat, ledit procédé comprenant les étapes consistant à :
 (a) fournir une solution non-aqueuse contenant un mélange de composés métalliques ayant une composition correspondant à celle des métaux dans l'oxyde métallique supraconducteur, lesdits composés métalliques étant choisis parmi les sels, les chélates, les halogénures, les hydroxydes, les peroxydes et les oxydes desdits métaux ;
 (b) appliquer ladite solution sur le substrat, pour former un film liquide ;
 (c) sécher ledit film liquide ; et
 (d) calciner ledit film séché pour convertir lesdits composés métalliques en une couche d'oxyde métallique supraconducteur.
2. Procédé selon la revendication 1, dans lequel ledit substrat se présente sous la forme d'un fil ou d'une plaque.
3. Procédé selon la revendication 1 ou la revendication 2, dans lequel lesdits composés métalliques sont des composés capables de former des oxydes lors d'une calcination à une température de 1000°C ou moins.
4. Procédé selon la revendication 3, dans lequel lesdits composés métalliques sont des naphthénates, des

octylates, des caprylates, des stéarates, des laurates, des butyrates, des propionates, des oxalates, des citrates, des lactates, des benzoates, des salicylates, des éthylènediaminetétraacétates, des nitrates, des carbonates, des chlorhydrates ou des acétylacétonates desdits métaux.

- 5 5. Procédé selon la revendication 3 ou la revendication 4, dans lequel l'étape (d) est effectuée à une température de 500 à 1000°C.
6. Procédé selon la revendication 5, dans lequel l'étape (d) est effectuée dans une atmosphère contenant de l'oxygène et pendant une durée de 0,5 heure ou plus.
- 10 7. Procédé selon la revendication 6, dans lequel la calcination dans l'atmosphère contenant de l'oxygène est précédée d'une calcination dans une atmosphère exempte d'oxygène.
8. Procédé selon l'une quelconque des revendications précédentes, dans lequel les étapes (a) à (d) sont répétées jusqu'à ce que ladite couche supraconductrice ait une épaisseur de 0,01 à 20 µm.
- 15 9. Procédé selon l'une quelconque des revendications précédentes, dans lequel ladite solution contient un premier composé choisi parmi les composés de l'yttrium, les composés du lanthane, les composés du néodyme, les composés du samarium, les composés de l'europium, les composés du gadolinium, les composés du dysprosium, les composés du holmium, les composés de l'erbium, les composés de l'ytterbium, les composés du lutécium et leurs mélanges, un deuxième composé choisi parmi les composés du baryum, les composés du strontium, les composés du calcium et leurs mélanges, et un composé du cuivre, de telle sorte que ledit oxyde métallique supraconducteur présente la formule :

$$AB_2Cu_3O_{7+x}$$
 dans laquelle A désigne Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb, Lu ou un mélange de deux ou plus de ceux-ci, B désigne Ba, Sr, Ca ou un mélange de deux ou plus de ceux-ci, et x désigne un nombre supérieur à -1 mais inférieur à +1.
- 20 10. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel ladite solution contient un composé du lanthane, un composé choisi parmi les composés du baryum, les composés du strontium, les composés du calcium et leurs mélanges, et un composé du cuivre, de telle sorte que ledit oxyde métallique supraconducteur présente la formule :

$$(La_{1-y}Z_y)_2CuO_{4-z}$$
 dans laquelle Z désigne Ba, Sr, Ca ou un mélange de deux ou plus de ceux-ci, y est supérieur à 0 mais n'est pas supérieur à 0,2, et z est un nombre inférieur à 1 mais non inférieur à 0.
- 25 11. Procédé selon l'une quelconque des revendications précédentes, dans lequel ledit substrat est constitué d'un métal, d'un oxyde métallique ou d'un matériau céramique.